

ARMY RESEARCH LABORATORY



An Initial Study of the Atmospheric Fate of Iodine From Halon Alternatives

Robert G. Daniel
Andrzej W. Mizolek
U.S. ARMY RESEARCH LABORATORY

Lian C. T. Shoue
Zeev B. Alfassi
Pedatsur Neta
Askar Fahr
Akshaya K. Nayak
Robert E. Huie

NATIONAL INSTITUTE OF STANDARDS AND TECHNOLOGY

ARL-TR-1155

July 1996

APPROVED FOR PUBLIC RELEASE; DISTRIBUTION IS UNLIMITED.

19960731 117

DTIC QUANTITY IMPRESSED 3

NOTICES

Destroy this report when it is no longer needed. DO NOT return it to the originator.

Additional copies of this report may be obtained from the National Technical Information Service, U.S. Department of Commerce, 5285 Port Royal Road, Springfield, VA 22161.

The findings of this report are not to be construed as an official Department of the Army position, unless so designated by other authorized documents.

The use of trade names or manufacturers' names in this report does not constitute indorsement of any commercial product.

REPORT DOCUMENTATION PAGE

*Form Approved
OMB No. 0704-0188*

Public reporting burden for this collection of information is estimated to average 1 hour per response, including the time for reviewing instructions, searching existing data sources, gathering and maintaining the data needed, and completing and reviewing the collection of information. Send comments regarding this burden estimate or any other aspect of this collection of information, including suggestions for reducing this burden, to Washington Headquarters Services, Directorate for Information Operations and Reports, 1215 Jefferson Davis Highway, Suite 1204, Arlington, VA 22202-4302, and to the Office of Management and Budget, Paperwork Reduction Project(0704-0188), Washington, DC 20503.

1. AGENCY USE ONLY (Leave blank)			2. REPORT DATE	3. REPORT TYPE AND DATES COVERED	
			July 1996	Final, Jun 93 - Dec 93	
4. TITLE AND SUBTITLE			5. FUNDING NUMBERS		
An Initial Study of the Atmospheric Fate of Iodine From Halon Alternatives			PR: 1L161102AH43		
6. AUTHOR(S)					
R. G. Daniel and A. W. Mizolek (USARL), L. C. T. Shoute,* Z. B. Alfassi,** P. Neta, A. Fahr, A. K. Nayak,* and R. E. Huie (NIST)					
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)			8. PERFORMING ORGANIZATION REPORT NUMBER		
U.S. Army Research Laboratory ATTN: AMSRL-WT-PC Aberdeen Proving Ground, MD 21005-5066			ARL-TR-1155		
9. SPONSORING/MONITORING AGENCY NAMES(S) AND ADDRESS(ES)			10. SPONSORING/MONITORING AGENCY REPORT NUMBER		
11. SUPPLEMENTARY NOTES					
* Permanent address: Bhabha Atomic Research Centre, Trombay, Bombay, India. ** Permanent address: Ben-Gurion University, Beer Shiva, Israel.					
12a. DISTRIBUTION/AVAILABILITY STATEMENT			12b. DISTRIBUTION CODE		
Approved for public release; distribution is unlimited.					
13. ABSTRACT (Maximum 200 words)					
One class of compounds being considered as replacements for the presently used Halons are iodinated fluorocarbons. This report addresses some of the outstanding questions regarding the atmospheric chemistry of these proposed alternative compounds and their by-products from either intentional or accidental release. Very little information on the atmospheric chemistry of iodinated compounds is known, thus this work fills a timely and pressing need to answer questions, such as, what are the ozone depletion potential (ODP) and global warming potential (GWP) of such compounds?					
14. SUBJECT TERMS			15. NUMBER OF PAGES		
halon alternatives, CF ₃ I, atmospheric compounds			16		
			16. PRICE CODE		
17. SECURITY CLASSIFICATION OF REPORT		18. SECURITY CLASSIFICATION OF THIS PAGE		19. SECURITY CLASSIFICATION OF ABSTRACT	
UNCLASSIFIED		UNCLASSIFIED		UNCLASSIFIED	
					20. LIMITATION OF ABSTRACT
					UL

INTENTIONALLY LEFT BLANK.

ACKNOWLEDGMENT

Research support from the U.S. Army Environmental Quality Basic Research Program is gratefully acknowledged.

INTENTIONALLY LEFT BLANK.

TABLE OF CONTENTS

	<u>Page</u>
ACKNOWLEDGMENT	iii
LIST OF FIGURES	vii
LIST OF TABLES	vii
1. INTRODUCTION	1
2. REACTIONS OF PERHALOALKYLPEROXYL RADICALS	1
3. EXPERIMENTAL SECTION	2
4. RESULTS AND DISCUSSION	4
4.1 Effect of Alkene Substituents on the Addition Reaction	4
4.2 Effect of Peroxyl Radical Substituents on the Addition Reaction	6
5. CF ₃ I PHOTOCHEMISTRY	6
6. CONCLUSION	9
7. REFERENCES	11
DISTRIBUTION LIST	13

INTENTIONALLY LEFT BLANK.

LIST OF FIGURES

<u>Figure</u>		<u>Page</u>
1.	Curve fits for three contributing transitions in CF ₃ I absorption	7
2.	Temperature dependent CF ₃ I absorption cross sections	8
3.	Schematic of the photochemistry experimental apparatus	8

LIST OF TABLES

<u>Table</u>		<u>Page</u>
1.	Rate Constants for Reactions of CF ₃ CCl ₂ O ₂ [·] , CCl ₃ O ₂ [·] , and CBr ₃ O ₂ [·] Radicals With Alkenes in Methanolic Solutions	5
2.	Rate Constants for Reactions of Haloalkylperoxy Radicals With Alkenes in Methanolic Solutions	7

INTENTIONALLY LEFT BLANK.

1. INTRODUCTION

There is a continuing and urgent need to establish the environmental acceptability and impact of new, military-specific candidate replacements for Halons and other ozone depleting compounds. This includes determining the atmospheric lifetimes, ozone depletion potential (ODP), global warming potential (GWP), and possible atmospheric production of toxic compounds. The recent requirements for the cessation of the sale and use of ozone depleting chemicals has created a new concern for the environmental impact of the use of replacement compounds. By design, most of these new replacement compounds have a much shorter atmospheric lifetime than the ozone depleting compounds. However, the products of their initial, or subsequent, atmospheric reactions may themselves be significant global warming gases. Specifically, this is the case if the parent compounds are highly fluorinated. These products of atmospheric reactions may also be quite toxic, and thus may present a threat to the ecosystem. Not surprisingly, relatively little research has been done so far to ascertain the impact on the lower atmosphere as a result of the use of replacement compounds because the transition to these replacement compounds is only now beginning. This report deals with two specific aspects of the atmospheric fate of certain candidate Halon replacement compounds. The first involves the study of reactivity of haloperoxy radicals, while the second involves the determination of the absorption cross sections for one of the leading Halon replacement candidate compounds, CF_3I .

2. REACTIONS OF PERHALOALKYLPEROXYL RADICALS

Most of the chemical compounds under consideration as possible replacements for the Halons and chlorofluorocarbons (CFCs) are expected to degrade in the atmosphere, either because they contain one or more C-H bonds which are subject to attack by atmospheric hydroxyl radicals, for example,



or because they may be photodissociated in the atmosphere, for example,



The resulting carbon-centered radical will rapidly react with oxygen to produce a halogenated peroxy radical



Subsequent reactions of the peroxy radical lead to the removal of the halogens from the atmosphere. There is, presently, a limited amount of information on the possible atmospheric reactions of these halogenated peroxy radicals. Peroxy radicals generally are expected to react with NO, NO₂, or with other peroxy radicals, including HO₂[·] (Wallington et al. 1992). Other reactions of peroxy radicals (e.g., with alkenes) generally are considered to be too slow to be of any importance in the atmosphere. Whereas this is clearly true for the nonhalogenated alkylperoxy radicals, halogenation may increase the reactivity of these radicals sufficiently so that other reaction pathways become important.

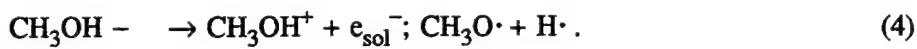
Formation and reactions of halogenated peroxy radicals might also relate to potential physiological effects of these halocarbon replacements. For example, the toxicity of CCl₄ has been suggested to arise from reactions of CCl₃O₂[·]; formed after the one-electron reduction of the parent. These peroxy radicals are strong oxidants and will react with antioxidants, such as vitamin C or vitamin E, but also may react with other physiological molecules, such as lipids, initiating damage (Slater 1978; Recknagel and Glende 1973; Brault 1985; Neta, Huie, and Ross 1990).

3. EXPERIMENTAL SECTION*

The rate constants for reactions of perhaloalkylperoxy radicals with the various alkenes in methanolic solutions were determined by pulse radiolysis. Air-saturated stock solutions containing 0.5–2% halocarbon and 1 × 10⁻⁴ – 5 × 10⁻³ mol L⁻¹ chlorpromazine were prepared for the liquid halocarbons. For the gaseous halocarbons, mixtures were prepared by adding a halocarbon-saturated chlorpromazine solution to oxygen-saturated methanol. A fresh sample of the solution was introduced into the irradiation cell with a syringe and was irradiated under aerobic conditions with a single pulse of 2-MeV electrons, with a dose of about 10 Gy.

The irradiation of methanol by ionizing radiation results in the formation of solvated electrons, radical cations, methoxyl radicals, and hydrogen atoms (Getoff et al. 1993; Dainton et al. 1969; Johnson and Salmon 1977).

* The mention of commercial equipment or material does not imply recognition or endorsement by the National Institute of Standards and Technology, nor does it imply that the material and equipment used are necessarily the best available for the purpose.



The radical cation will deprotonate,



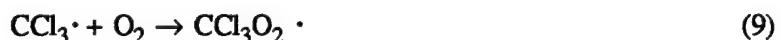
The hydrogen atom and the methoxyl radical will react with the solvent to produce the hydroxymethyl radical, with $k_6 = 2.6 \times 10^6 \text{ L mol}^{-1} \text{ s}^{-1}$ and $k_7 = 2.6 \times 10^5 \text{ L mol}^{-1} \text{ s}^{-1}$



Halogenated alkyl radicals are produced by the reduction of chlorine-, bromine-, or iodine-containing halocarbons by the solvated electron, for example:



In the presence of oxygen, haloalkylperoxy radicals are formed rapidly, $k_9 \sim 10^9 \text{ L mol}^{-1} \text{ s}^{-1}$ (Neta et al. 1990).



Although $\cdot\text{CH}_2\text{OH}$ is a reducing radical, it does not react rapidly with the haloalkenes used in this study and should react with oxygen to make the alkylperoxy radical $\text{HOCH}_2\text{O}_2\cdot$. This radical has much lower reactivity than the haloalkylperoxy radicals under investigation here and, therefore, does not interfere with these kinetic measurements (Neta et al. 1990).

In our pulse-radiolysis apparatus, reactions are monitored by kinetic spectrophotometry. Peroxyl radicals absorb only in the ultraviolet, primarily below 280 nm, and this absorption is not particularly strong. The same is true of any expected products of the reaction of these radicals with alkenes. With our apparatus, measurements are difficult in this spectral region, so, rather than following the reaction directly, we have determined the rate constants by competition kinetics using chlorpromazine (ClPz) as

a reference. The rate of oxidation of ClPz is determined directly by following the formation of the ClPz radical at 525 nm.



The addition of alkenes to solutions of ClPz leads to competition between reaction 10 and 11.



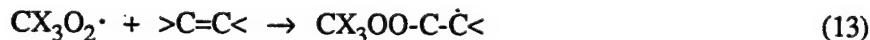
This will result in an enhanced rate of formation and decreased yield of ClPz^\cdot^+ . At constant ClPz concentration, the observed rate of formation of ClPz^\cdot^+ (k_{obs}) is given by:

$$k_{obs} = k_0 + k_1[\text{alkene}], \quad (12)$$

where k_0 is the first-order rate constant in the absence of alkene, which includes the rate of reaction 10 and any other loss processes for the peroxy radical except reaction 11, and k_1 is the second-order rate constant for reaction 11. The second-order rate constant is derived from the slope of a plot of the first-order rate constant against alkene concentration. At least three separate experiments were performed for each alkene concentration, and at least three alkene concentrations were employed for each alkene-radical reaction.

4. RESULTS AND DISCUSSION

4.1 Effect of Alkene Substituents on the Addition Reaction. The rate constants for the reactions of $\text{CF}_3\text{CCl}_2\text{O}_2^\cdot$ with 10 alkenes (Table 1) vary between 5×10^4 and $3 \times 10^7 \text{ L mol}^{-1} \text{ s}^{-1}$. The variation in rate constant with substituents about the double bond is consistent with addition as the main reaction path.



The same pattern was observed for the reactions of other halogenated peroxy radicals (Nahor and Neta 1991; Alfassi, Huie, and Neta 1993). The results for $\text{CCl}_3\text{O}_2^\cdot$ and $\text{CBr}_3\text{O}_2^\cdot$ are included in Table 1 for comparison. The conclusion that the primary reaction is electrophilic addition is based on the good

Table 1. Rate Constants for Reactions of $\text{CF}_3\text{CCl}_2\text{O}_2\cdot$; $\text{CCl}_3\text{O}_2\cdot$; and $\text{CBr}_3\text{O}_2\cdot$ Radicals With Alkenes in Methanolic Solutions

Compound	K, L mol ⁻¹ s ⁻¹			
	$\text{CF}_3\text{CCl}_2\text{O}_2\cdot$	$\text{CCl}_3\text{O}_2\cdot^a$	$\text{CBr}_3\text{O}_2\cdot^a$	σ^{*b}
2-buten-1-ol	4.9×10^4	2.5×10^4	2.3×10^4	1.54
3-methyl-3-buten-1-ol	9.3×10^4	5.0×10^4	5.0×10^4	1.16
3-methyl-2-buten-1-ol	3.3×10^5	1.6×10^5	1.2×10^5	1.05
cyclohexene	2.1×10^5	9.5×10^4	9.1×10^4	0.78
2-methyl-2-butene	2.8×10^6	1.3×10^6	—	0.49
1-methyl-1-cyclohexene	3.2×10^6	1.3×10^6	—	0.29
2,3-dimethyl-2-butene	3.1×10^7	1.4×10^7	1.0×10^7	0.00
2-methyl-3-ethyl-2-pentene	9.7×10^6	3.2×10^6	2.5×10^6	-0.20
1,2-dimethylcyclohexene	8.0×10^6	3.4×10^6	3.3×10^6	-0.20
styrene	5.7×10^5	3.2×10^5	2.1×10^5	2.07

^a (Alfassi, Huie, and Neta 1993) except for the results for 2-methyl-2-butene and 1-methyl-1-cyclohexane, which were measured in this study.

^b Taft σ^* substituent constants calculated as the sum of the individual σ^* values of the substituents on each double bond, taking: H = +0.49; CH₃ = -0.10; C₆H₅ = +0.60; CH₂OH = +0.56; CH₂CH₂OH = +0.18 (estimated from other values). For the cyclic alkenes, we calculated the values by assuming two open ends.

correlation observed between the logarithms of the rate constants and the Taft σ^* substituent constants. The values of σ^* , calculated as the sum of the individual values for the substituents on the double bond (Taft 1956), are included in Table 1. The correlation for the reactions of $\text{CF}_3\text{CCl}_2\text{O}_2\cdot$ with aliphatic alkenes and earlier similar correlations (Nahor and Neta 1991; Alfassi, Huie, and Neta 1993) shows considerable scatter. (Styrene, where the substituent effect may also involve resonance stabilization, is not included in the correlation.) Much better correlations are found, however, among the rate constants for the various peroxy radicals. We have determined the correlation between the rate constants for the reactions of $\text{CF}_3\text{CCl}_2\text{O}_2\cdot$ with the corresponding reactions of $\text{CCl}_3\text{O}_2\cdot$; and a similar correlation is observed with $\text{CBr}_3\text{O}_2\cdot$. The scatter in the σ^* plots points to a general tendency for the reactions of the peroxy radicals with the larger alkenes to be slower than expected. For example, the reactions of 2-methyl-3-ethyl-2-pentene and 1,2-dimethylcyclohexene are slower than the reaction of 2,3-dimethyl-2-butene, even though they have an equal degree of substitution and their σ^* values are more negative. These results indicate that there is a steric effect in the reactions of the larger alkenes with peroxy radicals.

4.2 Effect of Peroxyl Radical Substituents on the Addition Reaction. The results for a number of different haloperoxy radical reacting with five alkenes are presented in Table 2 (included, for comparison, are some results for $\text{CF}_3\text{O}_2^\cdot$; $\text{CCl}_3\text{O}_2^\cdot$; and $\text{CBr}_3\text{O}_2^\cdot$ from earlier work). It is clear that the trifluoromethylperoxy radical is more reactive than the trichloromethylperoxy radical, which is slightly more reactive than the tribromomethylperoxy radicals. Substitution of a single chlorine or bromine for a fluorine in $\text{CF}_3\text{O}_2^\cdot$ reduces the reactivity by a factor of 2. Substitution of two chlorine atoms for two fluorine atoms, as between $\text{CF}_3\text{CF}_2\text{O}_2^\cdot$ and $\text{CF}_3\text{CCl}_2\text{O}_2^\cdot$, leads to a reduction in reactivity of a factor of about 7. Substitution of a CF_3 group for an F atom does not have a clear effect: it doubles the rate constant for cyclohexene, but appears to be slightly deactivating for 2,3-dimethyl-2-butene and for 1,1-dimethyl cyclohexene. Substitution of two CF_3 groups leads to a result which appears even more anomalous: $\text{CF}_3\text{O}_2^\cdot$ and $(\text{CF}_3)_2\text{CFO}_2^\cdot$ react with cyclohexene with equal rate constants; for the more substituted alkenes, $\text{CF}_3\text{O}_2^\cdot$ is the more reactive. These results seem to suggest an effect of steric hindrance, which reduces the rate constants for the reactions of $\text{CF}_3\text{CF}_2\text{O}_2^\cdot$ with the larger alkenes and the rate constants for the reactions of $(\text{CF}_3)_2\text{CFO}_2^\cdot$ with all the alkenes.

5. CF_3I PHOTOCHEMISTRY

Trifluoriodomethane (CF_3I) is a leading Halon replacement candidate compound which is being considered as a drop-in replacement for Halon 1301. Unlike the situation with many of the perfluoro-(PFC), hydrofluoro- (HFC), and hydrochlorofluorocarbons (HCFC), the atmospheric chemistry of iodinated compounds is generally poorly understood. Presently, there are a number of data gaps in the photochemical behavior and reaction kinetics of iodinated compounds. One of the most important photophysical properties that affects the atmospheric lifetime, and thus the ODP and GWP, is the absorption cross section of the parent compound. This quantity is temperature dependent and, thus, has to be measured over a sufficiently wide temperature range. Figure 1 gives the result of recent measurements of the temperature dependent absorption cross section with the highest cross section curve at 340 nm corresponding to 333 K, while the lowest corresponds to 218 K. Figure 2 shows the three separate absorption bands that best fit the total absorption at the absorption peak. In addition, the quantum yield for formation of the photoproducts CF_3 and I atoms needs to be determined, since it can range between zero and one. These measurements are currently underway. Figure 3 shows the experimental setup for this work involving detection of CF_3 and CF_2 in the $1,250\text{--}1,275\text{ cm}^{-1}$ range.

Table 2. Rate Constants for Reactions of Haloalkylperoxyl Radicals With Alkenes^a in Methanolic Solutions

Radical	k, L mol ⁻¹ s ⁻¹				
	CH	MB	MCH	DMB	DMCH
CBr ₃ O ₂ ·	9.1 × 10 ^{4b}	—	—	1.0 × 10 ^{7b}	3.3 × 10 ^{6b}
CCl ₃ O ₂ ·	9.5 × 10 ^{4b}	1.3 × 10 ⁶	1.3 × 10 ⁶	1.4 × 10 ^{7b}	3.4 × 10 ^{6b}
CF ₃ O ₂ ·	7.5 × 10 ^{5b}	1.8 × 10 ⁷	1.7 × 10 ⁷	2.2 × 10 ^{8b}	7.5 × 10 ^{7b}
CF ₂ ClO ₂ ·	4.5 × 10 ⁵	9.4 × 10 ⁶	9.1 × 10 ⁶	8.3 × 10 ⁷	3.2 × 10 ⁷
CF ₂ BrO ₂ ·	4.9 × 10 ⁵	7.9 × 10 ⁶	7.7 × 10 ⁶	7.7 × 10 ⁷	2.7 × 10 ⁷
CF ₃ CCl ₂ O ₂ ·	2.1 × 10 ⁵	2.8 × 10 ⁶	3.2 × 10 ⁶	3.1 × 10 ⁷	8.0 × 10 ⁶
CF ₃ CF ₂ O ₂ ·	1.7 × 10 ⁶	1.9 × 10 ⁷	2.6 × 10 ⁷	1.3 × 10 ⁸	6.7 × 10 ⁷
(CF ₃) ₂ CFO ₂ ·	7.7 × 10 ⁵	6.8 × 10 ⁶	6.4 × 10 ⁶	5.0 × 10 ⁷	2.5 × 10 ⁷
·O ₂ CCl ₂ O ₂ ·	—	—	—	<1 × 10 ^{5c}	—

^a CH - cyclohexene, MB - 2-methyl-2-butene, MCH - 1-methylcyclohexene, DMB - 2,3-dimethyl-2-butene, DMCH - 1,2-dimethylcyclohexene.

^b Alfassi, Huie, and Neta (1993).

^c Addition of 124 mmol L⁻¹ DMB to a solution containing 4.8 mmol L⁻¹ chlorpromazine resulted in no measurable change in the rate of formation of the ClPz radical, suggesting that the rate constant for the reaction of ·O₂CCl₂O₂· with DMB is less than 10⁵ L mol⁻¹ s⁻¹.

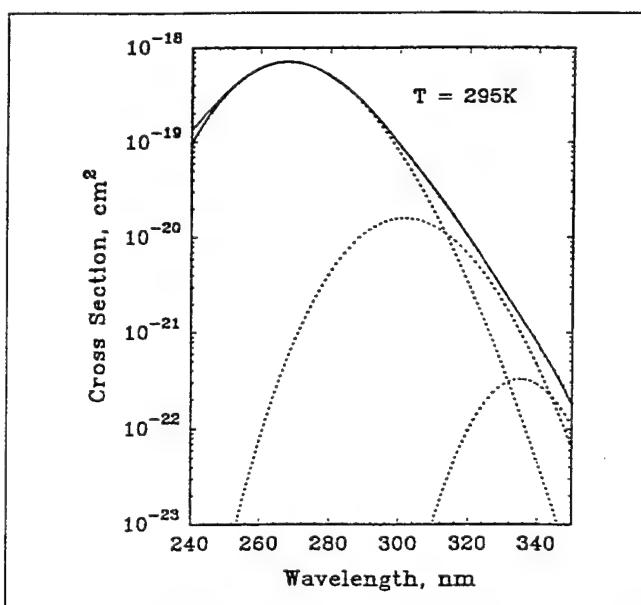


Figure 1. Curve fits for three contributing transitions in CF₃I absorption.

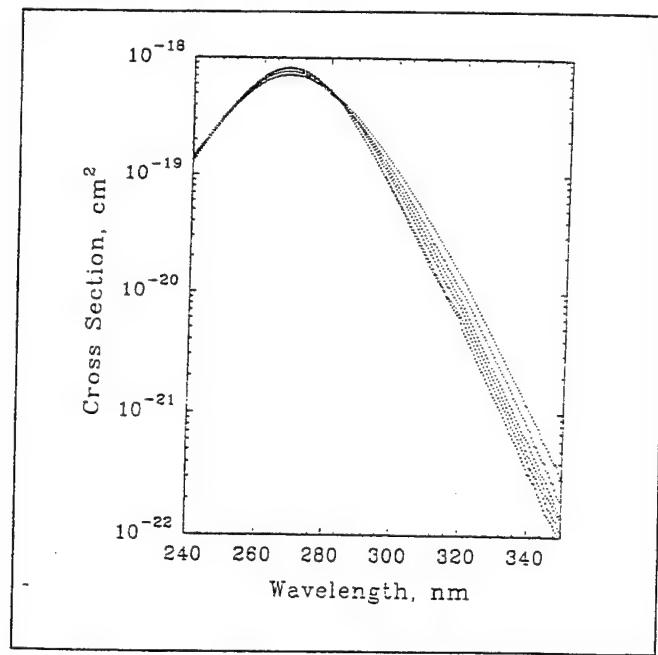


Figure 2. Temperature dependent CF_3I absorption cross sections.

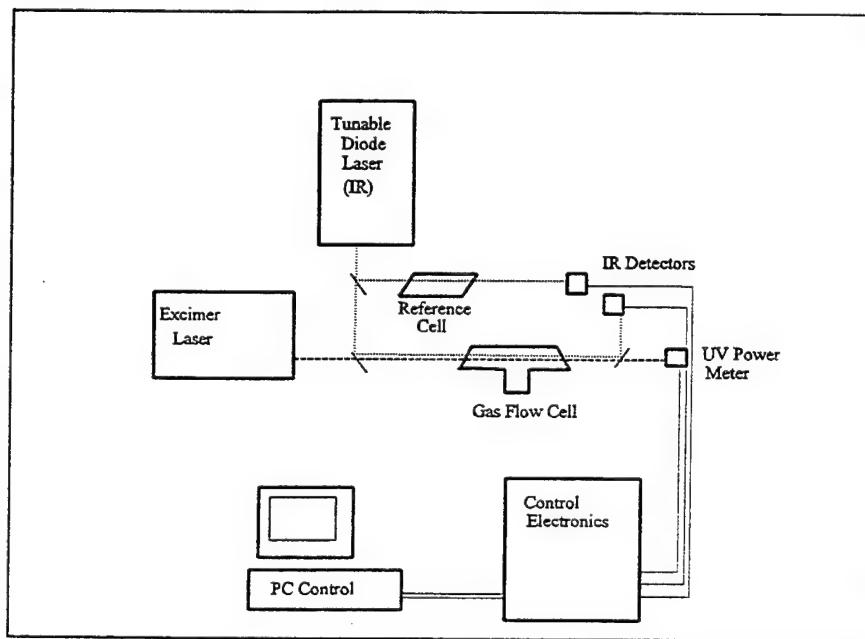


Figure 3. Schematic of the photochemistry experimental apparatus.

6. CONCLUSION

The gas-phase rate constant for the reaction of $\text{CF}_3\text{O}_2\cdot$ with NO is about $9 \times 10^9 \text{ L mol}^{-1} \text{ s}^{-1}$; the reaction of $\text{CF}_3\text{O}_2\cdot$ with NO_2 , at the high pressure limit, has a rate constant of about 4×10^9 (Wallington et al. 1992). In this work, we have found that the rate constants for the reactions of the halogenated peroxy radicals with alkenes in methanol reach a maximum at about $2 \times 10^8 \text{ L mol}^{-1} \text{ s}^{-1}$. We do not yet know the reactivity of halogenated peroxy radicals towards alkenes in the *gas phase*. The reactions of $\text{CCl}_3\text{O}_2\cdot$ with alkenes do show a variation in rate constant with solvent, but no particular correlation with solvent parameters was found (Alfassi, Huie, and Neta 1993). Rate constants for the reactions of some organic peroxy radicals derived from alcohols with nitric oxide were found to be similar in water and alcoholic solvents to those measured in the gas phase (Padmaja and Huie 1993).

The fact that the rate constants do not continue to increase with increasing fluorine substitution for the more reactive alkenes but, instead, decrease, suggests that the rate constants for the reactions of halogenated peroxy radicals with terpenes or other atmospheric alkenes will be at this value or lower. Therefore, the concentration of alkenes in the atmosphere must be at least 20–50 times greater than that of the nitrogen oxides for the reaction rates to be of equal magnitude. The concentration of nitrogen oxides are highly variable, with a global value of about 0.1–1 ppb. In urban areas, the concentration averages about 24 ppb (Graedel 1978). Alkene concentrations are also highly variable. Most measurements have been made in urban areas and range up to 20 ppb for individual branched-chain alkenes. (Ethene and propene have even higher concentrations; they are unlikely, however, to be reactive toward these peroxy radicals.) In rural areas, the concentrations of these alkenes, with the exception of isoprene, are likely to be much lower. Terpenes, however, are emitted in large quantities by vegetation. Ambient concentrations of 0.1–1 ppb have been reported near forests (Graedel 1978). Together, these data suggest that the concentrations of the nitrogen oxides and of the reactive alkenes are likely to be similar within a given area, probably within a factor of 10. This would indicate that the halogenated peroxy radicals are not likely to react with the alkenes, but will react with ambient NO and NO_2 .

INTENTIONALLY LEFT BLANK.

7. REFERENCES

- Alfassi, Z. B., R. E. Huie, and P. Neta. J. Phys. Chem., vol. 97, p. 6835, 1993.
- Brault, D. Enviro. Health Perspect., vol. 64, p. 53, 1985.
- Dainton, F. S., I. V. Janovsky, and G. A. Salmon. Chem. Comm., p. 335, 1969.
- Getoff, N., A. Ritter, F. Schworer, and P. Bayer. Radiat. Phys. Chem., vol. 41, p. 797, 1993.
- Graedel, T. E. Chemical Compounds in the Atmosphere. New York: Academic Press, 1978.
- Johnson, D. W., and G. A. Salmon. Can. J. Chem., vol. 55, p. 2030, 1977.
- Nahor, G., and P. Neta. Int. J. Chem. Kinet., vol. 23, p. 941, 1991.
- Neta, P., R. E. Huie, and A. B. Ross. J. Phys. Chem. Ref. Data, vol. 19, p. 413, 1990.
- Padmaja, S., and R. E. Huie. Biochem. Biophys. Res. Comm., vol. 195, p. 539, 1993.
- Recknagel, R. O., and E. A. Glende, Jr. CRC Crit. Rev. Toxicol., vol. 2, p. 263, 1973.
- Slater, T. F. Biochemical Mechanisms of Liver Injury. T. F. Slater, ed., Academic Press, London, 1978.
- Taft, R. W. Jr., Stearic Effects in Organic Chemistry. M. S. Newman, ed. New York: Wiley, p. 619, 1956.
- Wallington, T. J., P. Dagaut, and M. J. Kurylo. Chem. Rev., vol. 92, p. 667, 1992.

INTENTIONALLY LEFT BLANK.

<u>NO. OF COPIES</u>	<u>ORGANIZATION</u>
2	DEFENSE TECHNICAL INFO CTR ATTN DTIC DDA 8725 JOHN J KINGMAN RD STE 0944 FT BELVOIR VA 22060-6218
1	DIRECTOR US ARMY RESEARCH LAB ATTN AMSRL OP SD TA 2800 POWDER MILL RD ADELPHI MD 20783-1145
3	DIRECTOR US ARMY RESEARCH LAB ATTN AMSRL OP SD TL 2800 POWDER MILL RD ADELPHI MD 20783-1145
1	DIRECTOR US ARMY RESEARCH LAB ATTN AMSRL OP SD TP 2800 POWDER MILL RD ADELPHI MD 20783-1145

ABERDEEN PROVING GROUND

2 DIR USARL
ATTN AMSRL OP AP L (305)

<u>NO. OF COPIES</u>	<u>ORGANIZATION</u>	<u>NO. OF COPIES</u>	<u>ORGANIZATION</u>
1	HQDA ATTN SARD TT DR F MILTON PENTAGON WASHINGTON DC 20310-0103	2	COMMANDER US ARMY MISSILE COMMAND ATTN AMSMI RD PR E A R MAYKUT AMSMI RD PR P R BETTS REDSTONE ARSENAL AL 35809
1	HQDA ATTN SARD TT MR J APPEL PENTAGON WASHINGTON DC 20310-0103	1	OFFICE OF NAVAL RESEARCH DEPT OF THE NAVY ATTN R S MILLER CODE 432 800 N QUINCY ST ARLINGTON VA 22217
1	HQDA OASA RDA ATTN DR C H CHURCH PENTAGON ROOM 3E486 WASHINGTON DC 20310-0103	1	COMMANDER NAVAL AIR SYSTEMS COMMAND ATTN J RAMNARACE AIR 54111C WASHINGTON DC 20360
4	COMMANDER US ARMY RESEARCH OFFICE ATTN R GHIRARDELLI D MANN R SINGLETON R SHAW P O BOX 12211 RESEARCH TRIANGLE PARK NC 27709-2211	2	COMMANDER NAVAL SURFACE WARFARE CTR ATTN R BERNECKER R 13 G B WILMOT R 16 SILVER SPRING MD 20903-5000
1	DIRECTOR ARMY RESEARCH OFFICE ATTN AMXRO RT IP LIB SVCS P O BOX 12211 RESEARCH TRIANGLE PARK NC 27709-2211	5	COMMANDER NAVAL RESEARCH LAB ATTN M C LIN J McDONALD E ORAN J SHNUR R J DOYLE CODE 6110 WASHINGTON DC 20375
2	COMMANDER US ARMY ARDEC ATTN SMCAR AEE B D S DOWNS PICATINNY ARSENAL NJ 07806-5000	2	COMMANDER NAVAL WEAPONS CTR ATTN T BOGGS CODE 388 T PARR CODE 3895 CHINA LAKE CA 93555-6001
2	COMMANDER US ARMY ARDEC ATTN SMCAR AEE J A LANNON PICATINNY ARSENAL NJ 07806-5000	1	SUPERINTENDENT NAVAL POSTGRADUATE SCHOOL DEPT OF AERONAUTICS ATTN D W NETZER MONTEREY CA 93940
1	COMMANDER US ARMY ARDEC ATTN SMCAR AEE BR L HARRIS PICATINNY ARSENAL NJ 07806-5000	3	AL LSCF ATTN R CORLEY R GEISLER J LEVINE EDWARDS AFB CA 93523-5000

<u>NO. OF COPIES</u>	<u>ORGANIZATION</u>	<u>NO. OF COPIES</u>	<u>ORGANIZATION</u>
1	AFOSR ATTN J M TISHKOFF BOLLING AIR FORCE BASE WASHINGTON DC 20332	2	PRINCETON COMBUSTION RESEARCH LABS INC ATTN N A MESSINA M SUMMERFIELD PRINCETON CORPORATE PLAZA BLDG IV SUITE 119 11 DEERPARK DRIVE MONMOUTH JUNCTION NJ 08852
1	OSD SDIO IST ATTN L CAVENY PENTAGON WASHINGTON DC 20301-7100	3	DIRECTOR SANDIA NATL LABS DIVISION 8354 ATTN S JOHNSTON P MATTERN D STEPHENSON LIVERMORE CA 94550
1	COMMANDANT USAFAS ATTN ATSF TSM CN FORT SILL OK 73503-5600	1	BRIGHAM YOUNG UNIV DEPT OF CHEMICAL ENGINEERING ATTN M W BECKSTEAD PROVO UT 84058
1	UNIV OF DAYTON RSRCH INST ATTN D CAMPBELL AL PAP EDWARDS AFB CA 93523	1	CALIFORNIA INST OF TECH JET PROPULSION LAB ATTN L STRAND MS 233 103 4800 OAK GROVE DRIVE PASADENA CA 91109
1	NASA LANGLEY RESEARCH CTR ATTN G B NORTHAM MS 168 LANGLEY STATION HAMPTON VA 23365	1	CALIFORNIA INST OF TCHLGY ATTN F E C CULICK MC 301 46 204 KARMAN LAB PASADENA CA 91125
4	NATL BUREAU OF STANDARDS US DEPT OF COMMERCE ATTN J HASTIE M JACOX T KASHIWAGI H SEMERJIAN WASHINGTON DC 20234	1	UNIV OF CALIFORNIA LOS ALAMOS SCIENTIFIC LAB P O BOX 1663 MAIL STOP B216 LOS ALAMOS NM 87545
2	DIRECTOR LAWRENCE LIVERMORE NATL LAB ATTN C WESTBROOK W TAO MS L 282 P O BOX 808 LIVERMORE CA 94550	1	UNIV OF CA BERKELEY CHEMISTRY DEPARMENT ATTN C BRADLEY MOORE 211 LEWIS HALL BERKELEY CA 94720
1	DIRECTOR LOS ALAMOS NATL LAB ATTN B NICHOLS T7 MS B284 P O BOX 1663 LOS ALAMOS NM 87545	1	UNIV OF CA SAN DIEGO ATTN F A WILLIAMS AMES B010 LA JOLLA CA 92093

<u>NO. OF COPIES</u>	<u>ORGANIZATION</u>	<u>NO. OF COPIES</u>	<u>ORGANIZATION</u>
2	UNIV OF CA SANTA BARBARA QUANTUM INST ATTN K SCHOFIELD M STEINBERG SANTA BARBARA CA 93106	1	THE JOHNS HOPKINS UNIV CPIA ATTN T W CHRISTIAN 10630 LITTLE PATUXENT PKWY SUITE 202 COLUMBIA MD 21044-3200
1	UNIV OF COLORADO AT BOULDER ENGINEERING CTR ATTN J DAILY CAMPUS BOX 427 BOULDER CO 80309-0427	1	UNIV OF MICHIGAN GAS DYNAMICS LAB ATTN G M FAETH AEROSPACE ENGNRNG BLDG ANN ARBOR MI 48109-2140
3	UNIV OF SOUTHERN CA DEPT OF CHEMISTRY ATTN R BEAUDET S BENSON C WITTIG LOS ANGELES CA 90007	1	UNIV OF MINNESOTA DEPT OF MECHNCL ENGNRNG ATTN E FLETCHER MINNEAPOLIS MN 55455
1	CORNELL UNIV DEPT OF CHEMISTRY ATTN T A COOL BAKER LAB ITHACA NY 14853	4	PENNSYLVANIA STATE UNIV DEPT OF MECHNCL ENGNRNG ATTN K KUO M MICCI S THYNELL V YANG UNIVERSITY PARK PA 16802
1	UNIV OF DELAWARE CHEMISTRY DEPT ATTN T BRILL NEWARK DE 19711	2	PRINCETON UNIV FORRESTAL CAMPUS LIB ATTN K BREZINSKY I GLASSMAN P O BOX 710 PRINCETON NJ 08540
1	UNIV OF FLORIDA DEPT OF CHEMISTRY ATTN J WINEFORDNER GAINESVILLE FL 32611	1	PURDUE UNIV SCHL OF AERO & ASTRO ATTN J R OSBORN GRISSEY HALL WEST LAFAYETTE IN 47906
3	GEORGIA INST OF TECHLGY SCHOOL OF AEROSPACE ENGINEERING ATTN E PRICE W C STRAHLE B T ZINN ATLANTA GA 30332	1	PURDUE UNIV DEPT OF CHEMISTRY ATTN E GRANT WEST LAFAYETTE IN 47906
1	UNIV OF ILLINOIS DEPT OF MECH ENG ATTN H KRIER 144MEB 1206 W GREEN ST URBANA IL 61801	2	PURDUE UNIV SCHL OF MECHANICAL ENGNRNG ATTN N M LAURENDEAU S N B MURTHY TSPC CHAFFEE HALL WEST LAFAYETTE IN 47906

<u>NO. OF COPIES</u>	<u>ORGANIZATION</u>	<u>NO. OF COPIES</u>	<u>ORGANIZATION</u>
1	RENSSELAER POLYTCHNC INST DEPT OF CHEMICAL ENGNRG ATTN A FONTIJN TROY NY 12181	1	GENERAL APPLIED SCIENCE LABS INC 77 RAYNOR AVE RONKONKAMA NY 11779-6649
1	STANFORD UNIV DEPT OF MECHNCL ENGNRNG ATTN R HANSON STANFORD CA 94305	1	GENERAL ELECTRIC ORDNANCE SYSTEMS ATTN J MANDZY 100 PLASTICS AVE PITTSFIELD MA 01203
1	UNIV OF TEXAS DEPT OF CHEMISTRY ATTN W GARDINER AUSTIN TX 78712	1	GENERAL MOTORS RSCH LABS PHYSICAL CHEMISTRY DEPT ATTN T SLOANE WARREN MI 48090-9055
1	VA POLYTECH INST AND STATE UNIV ATTN J A SCHETZ BLACKSBURG VA 24061	2	HERCULES INC ATTN W B WALKUP E A YOUNT P O BOX 210 ROCKET CTR WV 26726
1	APPLIED COMBSTMN TECHLGY ATTN A M VARNEY P O BOX 607885 ORLANDO FL 32860	1	HERCULES INC ATTN R V CARTWRIGHT 100 HOWARD BLVD KENVIL NJ 07847
2	APPLIED MECHANICS REVIEWS ASME ATTN R WHITE & A WENZEL 345 E 47TH ST NEW YORK NY 10017	1	ALLIANT TECHSYSTEMS INC ATTN R E TOMPKINS MN 11 2720 600 SECOND ST NORTH HOPKINS MN 55343
1	TEXTRON DEFENSE SYSTEMS ATTN A PATRICK 2385 REVERE BEACH PKWY EVERETT MA 02149-5900	1	IBM CORPORATION RESEARCH DIVISION ATTN A C TAM 5600 COTTLE RD SAN JOSE CA 95193
1	BATTELLE TWSTIAC 505 KING AVE COLUMBUS OH 43201-2693	1	IIT RESEARCH INST ATTN R F REMALY 10 WEST 35TH ST CHICAGO IL 60616
1	COHEN PROFESSIONAL SVCS ATTN N S COHEN 141 CHANNING ST REDLANDS CA 92373	1	LOCKHEED MIS & SPACE CO ATTN GEORGE LO 3251 HANOVER ST DEPT 52 35 B204 2 PALO ALTO CA 94304
1	EXXON RESEARCH & ENG CO ATTN A DEAN ROUTE 22E ANNANDALE NJ 08801		

<u>NO. OF COPIES</u>	<u>ORGANIZATION</u>	<u>NO. OF COPIES</u>	<u>ORGANIZATION</u>
1	OLIN ORDNANCE ATTN V McDONALD LIB P O BOX 222 ST MARKS FL 32355-0222	3	THIOKOL CORPORATION WASATCH DIVISION ATTN S J BENNETT P O BOX 524 BRIGHAM CITY UT 84302
1	PAUL GOUGH ASSOCIATES INC ATTN P S GOUGH 1048 SOUTH ST PORTSMOUTH NH 03801-5423	1	UNITED TECHNOLOGIES RESEARCH CTR ATTN A C ECKBRETH EAST HARTFORD CT 06108
1	HUGHES AIRCRAFT CO ATTN T E WARD 8433 FALLBROOK AVE CANOGA PARK CA 91303	1	UNITED TECHNOLOGIES CORP CHEMICAL SYSTEMS DIV ATTN R R MILLER P O BOX 49028 SAN JOSE CA 95161-9028
1	SCIENCE APPLICATIONS INC ATTN R B EDELMAN 23146 CUMORAH CREST WOODLAND HILLS CA 91364	1	UNIVERSAL PROPULSION CO ATTN H J MCSPADDEN 25401 NORTH CENTRAL AVE PHOENIX AZ 85027-7837
3	SRI INTERNATIONAL ATTN G SMITH D CROSLEY D GOLDEN 333 RAVENSWOOD AVE MENLO PARK CA 94025	1	VERITAY TECHLGY INC ATTN E B FISHER 4845 MILLERSPORT HWY EAST AMHERST NY 14051-0305
1	STEVENS INST OF TECH DAVIDSON LAB ATTN R MCALEVY III HOBOKEN NJ 07030	1	FREEDMAN ASSOCIATES ATTN E FREEDMAN 2411 DIANA RD BALTIMORE MD 21209-1525
1	SVERDRUP TECHLGY INC LERC GROUP ATTN R J LOCKE MS SVR 2 2001 AEROSPACE PARKWAY BROOK PARK OH 44142	6	ALLIANT TECHSYSTEMS INC ATTN C CANDLAND L OSGOOD R BECKER J BODE R BURETTA M SWENSON 600 SECOND ST NE HOPKINS MN 55343
1	SVERDRUP TECHLGY INC ATTN J DEUR 2001 AEROSPACE PARKWAY BROOK PARK OH 44142	1	DIRECTOR US ARMY BENET LABS ATTN AMSTA AR CCB T SAM SOPOK WATERVLIET NY 12189
3	THIOKOL CORPORATION ELKTON DIVISION ATTN R BIDDLE R WILLER TECH LIB P O BOX 241 ELKTON MD 21921	8	NIST ATTN R HUIE CHEMISTRY A260 GAIITHERSBURG MD 20899

NO. OF
COPIES ORGANIZATION

ABERDEEN PROVING GROUND

33 DIR USARL
ATTN: AMSRL-WT-P, A HORST
AMSRL-WT-PC,
B E FORCH
R A PESCE-RODRIGUEZ
G F ADAMS
W R ANDERSON
R A BEYER
S W BUNTE
C F CHABALOWSKI
A COHEN
R F DANIEL
D DEVYNCK
J M HEIMERL
B HOMAN
A J KOTLAR
W F MCBRATNEY
K P MCNEILL-BOONSTOPPEL
K L MCNESBY
N E MEGHER
M S MILLER
A W MIZOLEK
J B MORRIS
J E NEWBERRY
R PASTEL
B M RICE
L SEGER
P V SHARMILA
R C SAUSA
M A SCHROEDER
W TEAGUE
J A VANDERHOFF
D VENIZELOS
A WHREN
H WILLIAMS

INTENTIONALLY LEFT BLANK.

USER EVALUATION SHEET/CHANGE OF ADDRESS

This Laboratory undertakes a continuing effort to improve the quality of the reports it publishes. Your comments/answers to the items/questions below will aid us in our efforts.

1. ARL Report Number/Author ARL-TR-1155 (Daniel) Date of Report July 1996
2. Date Report Received _____
3. Does this report satisfy a need? (Comment on purpose, related project, or other area of interest for which the report will be used.)

4. Specifically, how is the report being used? (Information source, design data, procedure, source of ideas, etc.)

5. Has the information in this report led to any quantitative savings as far as man-hours or dollars saved, operating costs avoided, or efficiencies achieved, etc? If so, please elaborate.

6. General Comments. What do you think should be changed to improve future reports? (Indicate changes to organization, technical content, format, etc.)

**CURRENT
ADDRESS**

Organization _____

Name _____

Street or P.O. Box No. _____

City, State, Zip Code _____

7. If indicating a Change of Address or Address Correction, please provide the Current or Correct address above and the Old or Incorrect address below.

**OLD
ADDRESS**

Organization _____

Name _____

Street or P.O. Box No. _____

City, State, Zip Code _____

(Remove this sheet, fold as indicated, tape closed, and mail.)
(DO NOT STAPLE)